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STPI/LARC: A 200°C POLYIMIDE ADHESIVE

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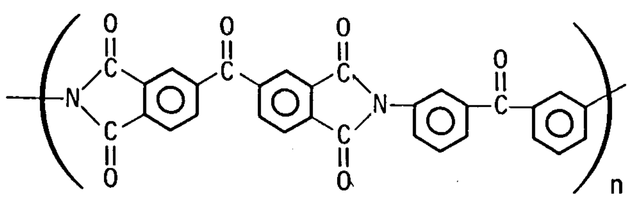
INTRODUCTION

Thermoplastic polyimides show potential for use as matrix resins and adhesives for aircraft applications. One such thermoplastic polyimide, LARC-TPI, was developed at NASA Langley Research Center in the late 1970's.[1,2]



LARC-TPI

Tg = 260°C

The thermoplastic behavior of this polymer has been attributed primarily to the flexibility of the aromatic diamine used in its preparation,[3] see Figure 1. This diamine, 3,3'-diaminobenzophenone, was not commercially available at the time LARC-TPI was shown to be an attractive adhesive system. Since the polymer did show considerable potential, several companies have investigated commercially feasible routes to make 3,3'-diaminobenzophenone. Presently, Mitsui Toatsu Chemicals, Incorporated in Japan* has a nonexclusive license to make LARC-TPI which it markets commercially.

The use of a meta-linked bridged diamine to make LARC-TPI appears to be a major factor in affording thermoplastic character to this polymer. Since these types of diamines are generally not commercially available at a

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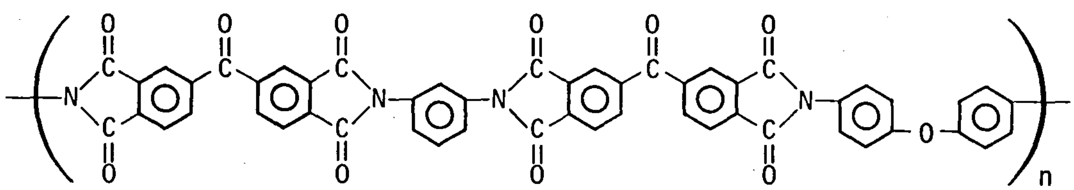
*Use of trade names or names of companies does not constitute an official endorsement by NASA, either expressed or implied.

reasonable cost, a program was begun to find a way to prepare a thermoplastic polyimide with properties similar to LARC-TPI using only commercially available materials. The system that shows the most promise to date is a random copolyimide with the following structure:



STPI/LARC

Tg = 283°C

The incorporation of two types of flexibilizing diamines in the polymer, designated STPI/LARC, affords a polyimide with thermoplastic properties similar to LARC-TPI, see Figure 2. Physical models of the LARC-TPI and the STPI/LARC were made and the two systems exhibited a similar degree of flexibility over several repeat units. These physical models made after reviewing the published work of I. K. Varma and B. S. Rao[4] on copolyimides led to the research in this study. The synthesis and characterization of this polymer and how it compares to the commercially available LARC-TPI is the subject of this paper.

EXPERIMENTAL

Materials. The chemicals were obtained from commercial sources. The list of chemicals and their source is as follows:

Benzophenonetetracarboxylic acid dianhydride (BTDA) - King Mar Laboratories
San Diego, CA

4,4'-Oxydianiline (ODA)	- Mallinckrodt, Inc. St. Louis, MO
Meta-phenylenediamine (MPD)	- Fluka Chemical Company Hauppauge, NY
N,N-Dimethylacetamide (DMAc)	- Fluka Chemical Company Hauppauge, NY
Phthalic anhydride (PA)	- Eastman Kodak Company Rochester, NY
2-Methoxyethyl ether (Diglyme)	- Aldrich Chemical Company Milwaukee, WI

Synthesis. The preparation of the STPI/LARC was carried out at room temperature in a 1000 ml cylindrical reaction flask with a removable, four-necked top. Stirring of the mixture was accomplished using an impeller blade driven by a constant-torque, overhead motor equipped with a variable speed control.

The BTDA (16.273g, 0.050M) and PA (0.270g, 0.002M) were slurried in a mixture of diglyme (35g) and DMAc (100g). To this was added ODA (5.006g, 0.025M) and the mixture was allowed to stir for 15 min to form a solution. Next the MPD (2.704g, 0.025M) was added and the solution was stirred for another 35 min. The resin was decanted from the vessel. An inherent viscosity of 0.52 dl/g was obtained for the resin.

Characterization. Lap shear strength was obtained according to ASTM D-1002 using a Model TT-C Instron Universal Testing Machine. The lap shear strengths reported represent an average of four lap shear specimens per test condition except where noted in Table 2. The range of the lap shear strengths is indicated by dashed lines in the bar graph figures and given in the tables. The average bondline thickness for STPI/LARC was 0.017 cm with a

range of 0.014 cm to 0.020 cm. Due to the greater flow of the LARC/TPI adhesive, average bondline thickness for the LARC-TPI was 0.009 cm with a range of 0.007 cm to 0.011. Specimens were heated in a clam-shell, quartz-lamp oven and were held at temperature for 10 minutes prior to testing. Temperatures were controlled to within ±3°C for all tests.

Glass transition temperatures (Tg) for the adhesive of fractured lap shear specimens were determined by thermomechanical analysis (TMA) on a DuPont Analyzer in static air at a heating rate of 5°C/min using a hemispherical probe with a 15g load.

Inherent viscosity measurements were made at 35°C using a Cannon Ubbelohde viscometer on 0.5% solutions in DMAc.

Adhesive Bonding. Adhesive tape for the STPI/LARC was prepared by brush coating a primer solution of polyamic-acid, diluted to approximately 7.5 wt% solids in diglyme/DMAc, onto 112 E-glass cloth with A-1100 finish (γ-aminopropylsilane). The glass cloth had been tightly mounted on a metal frame and dried in a forced-air oven for 30 min at 100°C prior to coating. The 0.01 cm thick glass cloth served as a carrier for the adhesive as well as for bondline control and an escape channel for solvent. The coated cloth was then air-dried for 1 hr and heated for 1 hr at each of three temperatures: 100°C, 150°C, and 175°C. Subsequently each application of a 15 wt% solids solution was brush coated onto the cloth and exposed to the following schedule until a thickness of 0.020 - 0.025 cm was obtained:

(1) Room temperature, hold 1 hr

(2) RT → 100°C, hold 1 hr

(3) 100°C → 150°C, hold 2 hrs

(4) 150°C → 175°C, hold 3 hrs

The involved procedure to prepare the tape was necessary to drive-off solvent and reaction product volatiles when converting the polyamic-acid resin to the polyimide. Imidization of polyamic-acids to polyimides generally occurs above 160°C with the degree of conversion being a function of time and temperature.

Adhesive tape for the LARC-TPI was prepared in a similar manner to the STPI/LARC in an attempt to normalize the tape preparations. LARC-TPI, Lot No. 26-001, was supplied by Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan, as a 29.1 wt% solids polyamic-acid solution in diglyme with an inherent viscosity of 0.54 dl/g (35°C). Brookfield viscosity was 24,600 cps (23°C). A solution, diluted to approximately 7.5 wt% solids, was applied as the primer to the glass cloth and treated as above. Due to the difficulty of applying the as-supplied 29.1 wt% solids solution, it was necessary to dilute the solution to approximately 24 wt% solids for easier application by brush to the glass cloth. Heat treatment of the applied resin solution was the same as that for STPI/LARC except fewer applications were necessary due to the higher solids content of the LARC-TPI solution. The adhesive tape thus prepared foamed slightly.

The prepared adhesive tapes were used to bond titanium adherends (Ti 6AL-4V, per Mil-T-9046E, Type III Comp. C) with a nominal thickness of 0.13 cm. The Ti(6AL-4V) panels were grit blasted with 120 grit aluminum oxide, washed with methanol, and treated with a Pasa-Jell 107* treatment to form a stable oxide on the surface. The adherends were washed with water and dried

*Trade name for a titanium surface treatment available from Semco, Glendale, CA.

in a forced-air oven at 100°C for 5 min. The treated adherends were primed within two hours of the surface treatment by applying a thin coat of the polyamic-acid solution of the respective adhesives on the surfaces to be bonded. After air-drying in a forced-air oven for 30 min, they were heated for 15 min at 100°C and 15 min at 150°C. The primed adherends were stored in a polyethylene bag and placed in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 1.27 cm overlap (ASTM D-1002) and applying 2.1 MPa pressure in a hydraulic press during the heating schedule. Bonding temperature was monitored using a type K thermocouple spot-welded to the titanium adherend at the edge of the bondline.

The following bonding cycles for the STPI/LARC adhesive were investigated during this study to determine a bonding process which produced good strengths.

Cycle 1

(1) 2.1 MPa pressure, heating rate ≈ 8.2°C/min, RT → 329°C

(2) Hold 15 min at 329°C

(3) Cool under pressure to ≈ 150°C and remove from bonding press

Cycle 2

Same as Cycle 1 except RT → 343°C

Cycle 3

Same as 1 except RT → 343°C, hold 1 hr

A bonding cycle was selected from the above conditions and used to determine the effects of an additional heat treatment of the STPI/LARC adhesive tape prior to bonding based on the lap shear strengths. Next, lap shear

specimens were prepared for thermal exposure for 500 and 1000 hours at 204°C. Thermal exposure was performed in a forced-air oven controlled within ±1% of exposure temperature. Lap shear tests were conducted at room temperature, 177°C, and 204°C before (controls) and after exposure.

A 72-hour water-boil test was conducted in laboratory glassware containing boiling distilled water. The bonded area of the lap shear specimens was immersed during the 72-hour period. Lap shear strengths were subsequently determined at room temperature, 177°C, and 204°C.

The bonding cycle selected for the STPI/LARC was also used to prepare lap shear specimens with the LARC-TPI adhesive tape. The thermal exposure in air and water-boil exposure tests were the same as that for the STPI/LARC.

RESULTS AND DISCUSSION

Materials. The chemicals for this program were of very high purity which in most cases allowed them to be used without further purification. The BTDA from King Mar Laboratories was originally prepared by Gulf Chemical (now Allco). King Mar Laboratories purified this material by recrystallizing it from a 90:10 mixture of anisole/acetic anhydride. The ODA from Mallinkrodt was a high purity grade. In some cases, where this material had aged in the light, a darkening occured. This ODA was sublimed in order to obtain the original purity. MPD from Fluka is an off-white crystalline material supplied in an opaque bottle. Prolonged exposure of this chemical to air and/or light will result in a severe darkening. The other three chemicals, DMAc, PA, and diglyme, are all capable of absorbing water if they

are left open to the atmosphere for extended times. Water is, of course, deleterious to the reaction and usually results in a lower inherent viscosity (molecular weight).

Synthesis. The reaction scheme for STPI/LARC is shown in Figure 2. The BTDA and PA had only partial solubility in the mixed solvent system of DMAc and diglyme. The BTDA is the difunctional anhydride which allows for molecular weight buildup (chain growth). The PA was used as a method of controlling the molecular weight so that the level was high enough to yield a tough, flexible polymer, but not so high as to inhibit the thermoplastic flow properties. The resulting polymer did afford a flexible film when cast and cured to 300°C. There was adequate thermoplastic flow as evidenced by the softening that occurred during the adhesive bonding operation.

The ODA was added initially because in a preliminary experiment a precipitation occurred when MPD was added first. Also, in preparing a random copolymer by the method that was used, there is no way of ensuring that block formation does not occur. From a statistical standpoint this should not occur, but previous work in our laboratory has shown that diglyme may promote this behavior. For this reason, a mixture of diglyme and DMAc was used in an effort to avoid block formation and to improve solubility.

Bond Cycle Selection. Adhesive tape for the STPI/LARC was used to bond lap shear specimens using the three cycles mentioned previously. The bonding pressure was held constant for the three cycles while the temperature and time-held-at-temperature varied. A higher than normal bonding pressure, 2.1 MPa, was used to assure sufficient flow of the polymer during bonding. Results on the effects of the bond cycle are given in Table 1 and shown in Figure 3. Lap shear strengths were determined at RT, 177°C,

and 204°C. Results indicate very little difference in strengths for the three test temperatures. Average strengths at RT for the three cycles ranged from 22.2 to 25.4 MPa; at 177°C, from 23.9 to 25.8 MPa; and at 204°C, from 24.3 to 26.7 MPa. The RT test specimens failed primarily adhesively for all three cycles, changing to cohesive with increasing test temperature. The Tg's, measured on the fractured RT test specimens, tended to increase as temperature and time-held-at-temperature increased, i.e. Cycle 1, 222°C; Cycle 2, 240°C; and Cycle 3, 266°C. Because all three cycles produced essentially the same lap shear strengths and because Cycle 3 had the highest Tg, 266°C, it was selected as the bonding cycle for use in the remainder of this study.

Past experience with these types of thermoplastic polyimides had shown a beneficial effect when heating the adhesive tape to higher temperatures for a period of time.[5] Table II and Figure 4 show the effect on lap shear strength resulting from an additional heating of the adhesive tape prior to bonding. Specimens were bonded after each of the successive heat treatments, i.e. 1 hr at 200°C, plus 1 hr at 225°C, and plus 1 hr at 250°C. Again lap shear strengths were determined at RT, 177°C, and 204°C. No significant difference in strengths were obtained at any test temperature due to the heat treatment of the adhesive tape. In fact, the average strength was essentially the same for all test temperatures and tape heat treatments. The Tg's determined were also about the same, 265 - 267°C, as that of the adhesive tape used prior to the additional heat treatment, 266°C. The significant difference found was that the type of failure for the adhesive tape taken to 250°C for 1 hr was cohesive at all test temperatures, whereas, others changed from an adhesive failure to a cohesive

failure. Due to the cohesive type of failure for the adhesive tape taken to 250°C for 1 hr, it was used for the STPI/LARC adhesive tape treatment to prepare lap shear specimen for the thermal exposure and water-boil tests.

Adhesive tape for the LARC-TPI was prepared in a similar manner to the STPI/LARC except no additional heat treatment above the 175°C for 3 hrs was performed. Cycle 3 was also used to fabricate lap shear specimens of LARC-TPI for the thermal exposure and water-boil tests.

Thermal Exposure Tests. The stability of the adhesives to long term thermal exposure was determined for both adhesive systems by exposing lap shear specimens for 500 and 1000 hrs at 204°C in a forced-air oven. Cycle 3 (2.17 MPa pressure, RT to 343°C, hold 1 hr) was used to bond the lap shear specimens for the thermal exposure study. Lap shear strengths were determined at RT, 177°C, and 204°C before (controls) and after exposure.

Results for STPI/LARC are given in Table III and Figure 5. Little change in lap shear strength was observed due to the thermal exposure. The 500 and 1000 hr exposure strengths, approximately 23 MPa, are the same, but slightly lower than the control strengths, approximately 26 MPa. The primary failure mode of the fractured specimens was cohesive except for the 500 and 1000 hr exposure specimens tested at RT which were adhesive/cohesive and adhesive, respectively. The Tg's measured on the fractured adhesive surfaces were between 260°C and 267°C.

Results are given in Table IV and Figure 6 for the LARC-TPI adhesive. No significant difference was found in the lap shear strength with time of thermal exposure for any one temperature (RT, 32.9 - 34.1 MPa; 177°C, 29.0 - 29.9 MPa; and 204°C, 25.2 - 27.8 MPa). In all cases there is a general trend of decreasing lap shear strength with increasing test temperature,

however the decrease is small, less than 24% for up to a 204°C test temperature, when compared to most adhesive systems for this temperature range. All failures were 100% cohesive. There appears to be a slight increase in Tg with thermal aging which is characteristic for these types of adhesives (polyimides).

Both adhesive systems show promising results for the thermal exposure investigated. Higher overall lap shear strengths were obtained for the LARC-TPI adhesive system as compared to the STPI/LARC system but the STPI/LARC had the higher Tg's which generally indicates a higher potential use temperature. Limited tests at 232°C of LARC-TPI have shown lap shear strengths of 1.61 MPa, however strengths were not determined at this temperature for the STPI/LARC. All failures for the LARC-TPI were 100% cohesive, whereas, the STPI/LARC failed primarily cohesively with partial adhesive failure.

72-Hour Water-boil. The resistance of the two adhesives to water (humidity) was determined by immersing lap shear specimens in distilled boiling water for a 72-hour period and subsequently testing their lap shear strengths at RT, 177°C, and 204°C. Results of those tests are given in Table V and Figure 7 for the STPI/LARC adhesive system and in Table VI and Figure 8 for the LARC-TPI system.

The lap shear strengths of STPI/LARC specimens after water-boil were 88% of the control's RT strength, 62% of the control's 177°C strength, and 68% of the control's 204°C strength. The lap shear strengths for the LARC-TPI were 84% of the control's RT strength, 67% of the control's 177°C strength, and 40% of the control's 204°C strength. From these results, it appears that the STPI/LARC adhesive system retains a higher percentage of

strength for the 204°C test, whereas for the RT and 177°C tests, they both retain approximately the same percentage of the control strengths. All failures were primarily cohesive. Essentially no changes were measured for the Tg's after the water-boil for the STPI/LARC and LARC-TPI adhesive systems.

The LARC-TPI initially provided higher lap shear strengths for all tests, except one, the STPI/LARC retained a higher strength at 204°C after water-boil than the LARC-TPI, 17.0 MPa compared to 10.1 MPa.

Comparison of LARC-TPI with Literature Data. A comparison of the present LARC-TPI data with data from Boeing Aerospace Company (BAC) is given in Table VII.[2]

Although BAC used a different surface preparation, the chromic acid anodize treatment, the maximum temperature used during the bonding cycle, 343°C, was the same. The RT lap shear strengths were about the same, 33.0 MPa for the present study compared to 29.7 MPa for the BAC tests. The tests at 232°C also produced similar results, 15.8 MPa for the present study and 14.8 MPa for BAC. Failure modes were not reported by BAC whereas the test specimens of the present study failed cohesively. More recent data generated by BAC has shown excellent strength retention to thermal exposure in-air at 232°C for up to 37,000 hrs.[6]

CONCLUSIONS

A thermoplastic polyimide, LARC-TPI, has previously been shown to be an excellent adhesive for several applications. The reason for the thermoplastic nature of this polymer has been attributed to the flexibility of the

backbone caused by the use of the meta-linked diamine - 3,3'-diaminobenzophenone.

In this work the use of a combination of two flexibilizing diamines in a polymer, STPI/LARC, has resulted in a copolyimide with adhesive performance that is very similar to LARC-TPI. The experimental data on a commercially available LARC-TPI and on the experimental STPI/LARC show both systems to possess exceptional lap shear strengths at room and elevated temperatures up to 204°C both before and after aging at 204°C. However, the LARC-TPI strengths were, in general, higher than corresponding STPI/LARC strengths. After a 72-hour water-boil exposure, bonded specimens of both systems exhibited similar percentage strength losses for room temperature and 177°C tests. In contrast, the STPI/LARC retained a much higher percentage of its original strength when tested at 204°C after the water-boil exposure (68% versus 40% retention). This phenomenon was most likely the result of STPI/LARC having a higher glass transition temperature than LARC-TPI (24°C difference).

An attractive feature of the STPI/LARC is that is was prepared from relatively inexpensive, commercially available chemicals. Therefore, this flexible, thermoplastic copolyimide shows considerable potential as an adhesive based on this initial study and because of its ease of preparation with low cost, commercially available materials.

REFERENCES

1. A. K. St. Clair and T. L. St. Clair, "A Multipurpose Thermoplastic Polyimide", 26th National SAMPE Symposium Preprints, 26, 165 (1981).

2. S. G. Hill, P. D. Peters, and C. L. Hendricks, "Evaluation of High Temperature Structural Adhesives for Extended Service", NASA Contractor Report 165944, July 1982.

3. V. L. Bell, B. L. Stump, and H. Gager, "Polyimide Structure-Property Relationships. II. Polymers from Isometric Diamines", J. of Polymer Science: Polymer Chemistry Edition, 14, 2275 (1976).

4. I. K. Varma and B. S. Rao, "Polyimides. II. Effect of Structure on Properties of Polyimides", J. of Polymer Science: Polymer Letters Edition, 26, 545 (1981).

5. D. J. Progar, "Processing Study of a Polyimidesulfone Adhesive", NASA TM 85742 (1984).

6. C. L. Hendricks, "High Temperature Adhesive Development and Evaluation", The Second Symposium on Welding, Bonding, and Fastening, Langley Research Center, Hampton, VA, October 1984.

Table I. Effects of Bonding Cycle on LSS for STPI/LARC Bonded TI 6-4.

BONDING CYCLE	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE*	Tg** °C
1	2	RT	25.4	24.6 - 26.1	AD	222
	3	177	25.5	22.1 - 28.3	CO	--
	3	204	25.9	24.9 - 26.7	CO	--
2	3	RT	25.0	20.0 - 29.1	AD	240
	4	177	25.8	22.5 - 28.0	CO	--
	3	204	26.7	26.2 - 27.0	CO	--
3	4	RT	22.2	20.7 - 24.3	AD	266
	4	177	23.9	22.2 - 27.2	CO/AD	--
	4	204	24.3	21.2 - 26.2	CO	--

* AD - adhesive

CO - cohesive (through glass cloth)

** Glass transition temperature, single measurement. Tg determined by TMA on a STPI/LARC film cured to 300°C was 283°C.

Table II. Effect on LSS of Additional Heat Treatment to STPI/LARC Adhesive Tape.

ADDITIONAL HEAT TREATMENT*	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE**	Tg,*** °C
1 HR AT 200°C	4	RT	24.6	23.1 - 25.8	AD	265
	4	177	25.2	24.3 - 26.0	CO/AD	--
	4	204	26.2	24.5 - 27.8	CO	--
AS ABOVE PLUS 1 HR AT 225°C	4	RT	25.0	24.1 - 26.8	AD	265
	4	107	26.7	25.7 - 28.0	CO	--
	4	204	26.3	25.4 - 27.6	CO	--
AS ABOVE PLUS 1 HR AT 250°C	4	RT	26.6	24.2 - 29.6	CO	267
	4	107	27.0	23.6 - 30.0	CO	--
	4	204	25.0	24.1 - 26.0	CO	--

* Prior adhesive tape treatment was heating in forced-air oven at 100°C, 150°C, and 175°C after each application until ≈ 0.025 cm thick

** AD - adhesive

CO - cohesive (through glass cloth)

*** Glass transition temperature, single measurement

Table III. Effects of Thermal Exposure (in Air) on LSS for STPI/LARC Bonded Ti 6-4.

THERMAL EXPOSURE AT 204°C, HR	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE*	Tg,** °C
0 [CONTROLS]	4	RT	26.6	24.2 - 29.6	CO	267
	4	177	27.0	23.6 - 30.0	CO	--
	4	204	25.0	24.1 - 26.0	CO	--
500	4	RT	23.2	20.0 - 25.0	AD/CO	265
	4	107	23.9	23.2 - 24.6	CO	--
	4	204	23.4	22.4 - 24.5	CO	--
1000	4	RT	24.1	23.6 - 25.1	AD	260
	4	107	23.2	22.1 - 25.0	CO	--
	4	204	22.7	20.7 - 24.1	CO	--

* AD - adhesive

CO - cohesive (through glass cloth)

** Glass transition temperature, single measurement

Table IV. Effects of Thermal Exposure (in Air) on LSS for LARC-TPI Bonded Ti 6-4.

THERMAL EXPOSURE AT 204°C, HR	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE*	Tg,** °C
0	4	RT	33.0	32.3 - 33.5	CO	228
[CONTROLS]	4	177	29.5	28.8 - 30.7	CO	225
	4	204	25.2	25.0 - 25.4	CO	236
500	4	RT	34.1	32.7 - 35.3	CO	242
	4	107	29.0	27.5 - 30.5	CO	242
	4	204	26.9	26.6 - 27.1	CO	237
1000	4	RT	32.9	32.3 - 34.4	CO	242
	4	107	29.9	28.5 - 31.0	CO	246
	4	204	27.8	27.2 - 28.6	CO	238

* AD - adhesive
CO - cohesive

** Glass transition temperature, single measurement. Tg determined by TMA on a LARC-TPI film cured to 300°C was 259°C.

Table V. Effect of 72-Hour Water-Boil on LSS for STPI/LARC Bonded Ti 6-4.

	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE*	Tg,** °C
CONTROLS	4	RT	26.6	24.2 - 29.6	CO	267
	4	177	27.0	23.6 - 30.0	CO	--
	4	204	25.0	24.1 - 26.0	CO	--
72-HOUR WATER-BOIL	4	RT	23.3	20.8 - 25.2	CO	265
	4	107	16.9	14.8 - 18.1	CO	264
	4	204	17.0	16.7 - 17.5	CO	257

* AD - adhesive

CO - cohesive (through glass cloth)

** Glass transition temperature, single measurement

Table VI. Effect of 72-Hour Water-Boil on LSS for LARC-TPI Bonded Ti 6-4.

	NUMBER OF SPECIMENS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	RANGE OF LSS, MPa	PRIMARY FAILURE MODE*	Tg,** °C
CONTROLS	4	RT	33.0	32.3 - 33.5	CO	228
	4	177	29.5	28.8 - 30.7	CO	225
	4	204	25.2	25.0 - 25.4	CO	236
72-HOUR WATER-BOIL	4	RT	27.8	26.7 - 28.8	CO	239
	4	107	19.7	19.1 - 20.3	CO	230
	4	204	10.1	9.4 - 11.0	CO	225

* AD - adhesive

CO - cohesive

** Glass transition temperature, single measurement

Table VII. Comparison of LARC-TPI Lap Shear Strength Data

DATA SOURCE	SURFACE TREATMENT	BONDING CONDITIONS	TEST TEMPERATURE, °C	AVERAGE LSS, MPa	PRIMARY FAILURE MODE
Present Study	PASA-JELL 107	2.1 MPa; 8°C/min, RT → 343°C, hold 343°C, 60 min	RT 232	33.0 15.8	CO* CO
REF. 2	Chromic Acid Anodize (CCA)	1.38 MPa, 2-3°C/min; RT → 343°C, hold 90 min; postcure 2 hrs at 316°C	RT 232	29.7 14.8	-- --

*CO - cohesive

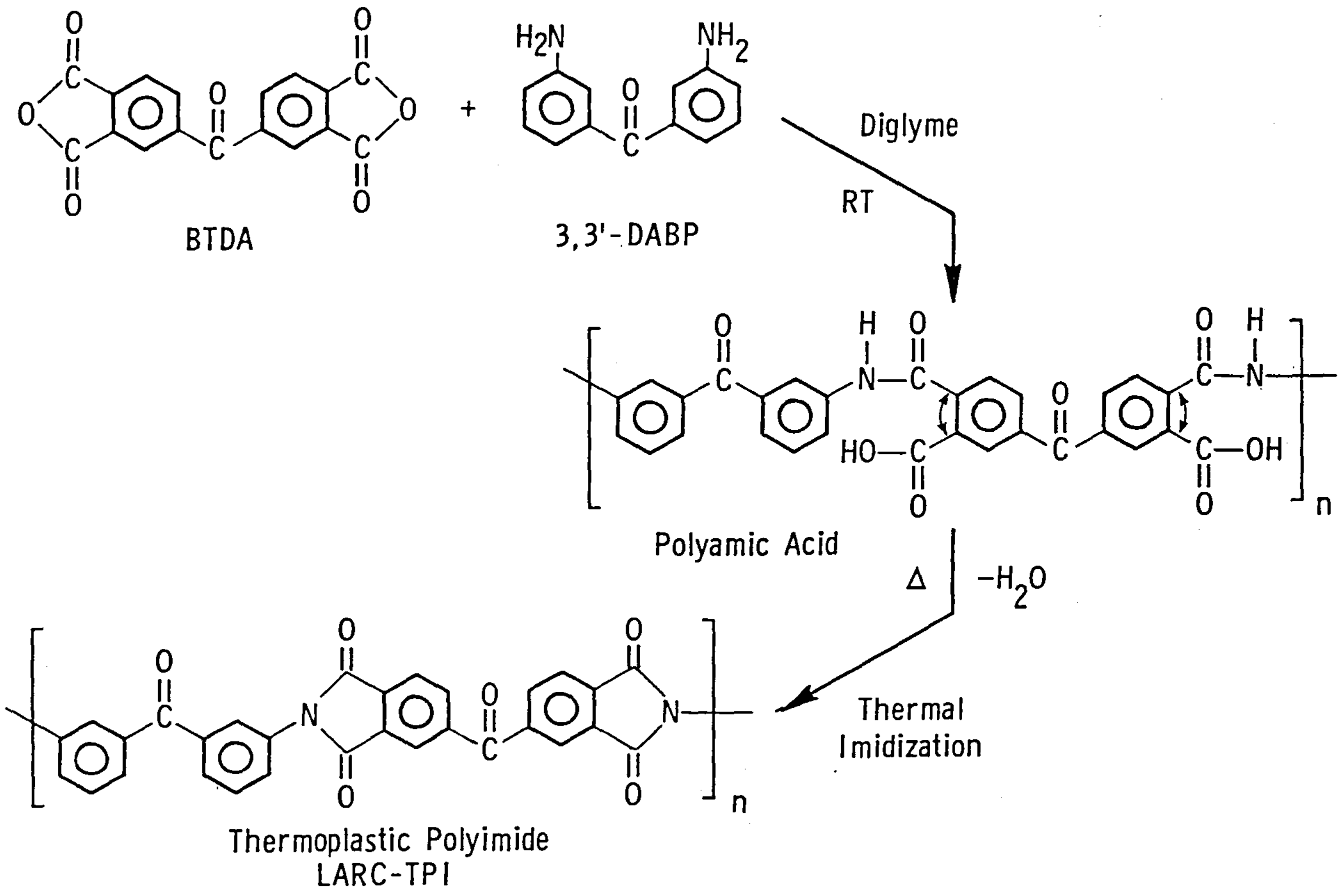


Figure 1. Reaction scheme for LARC-TPI

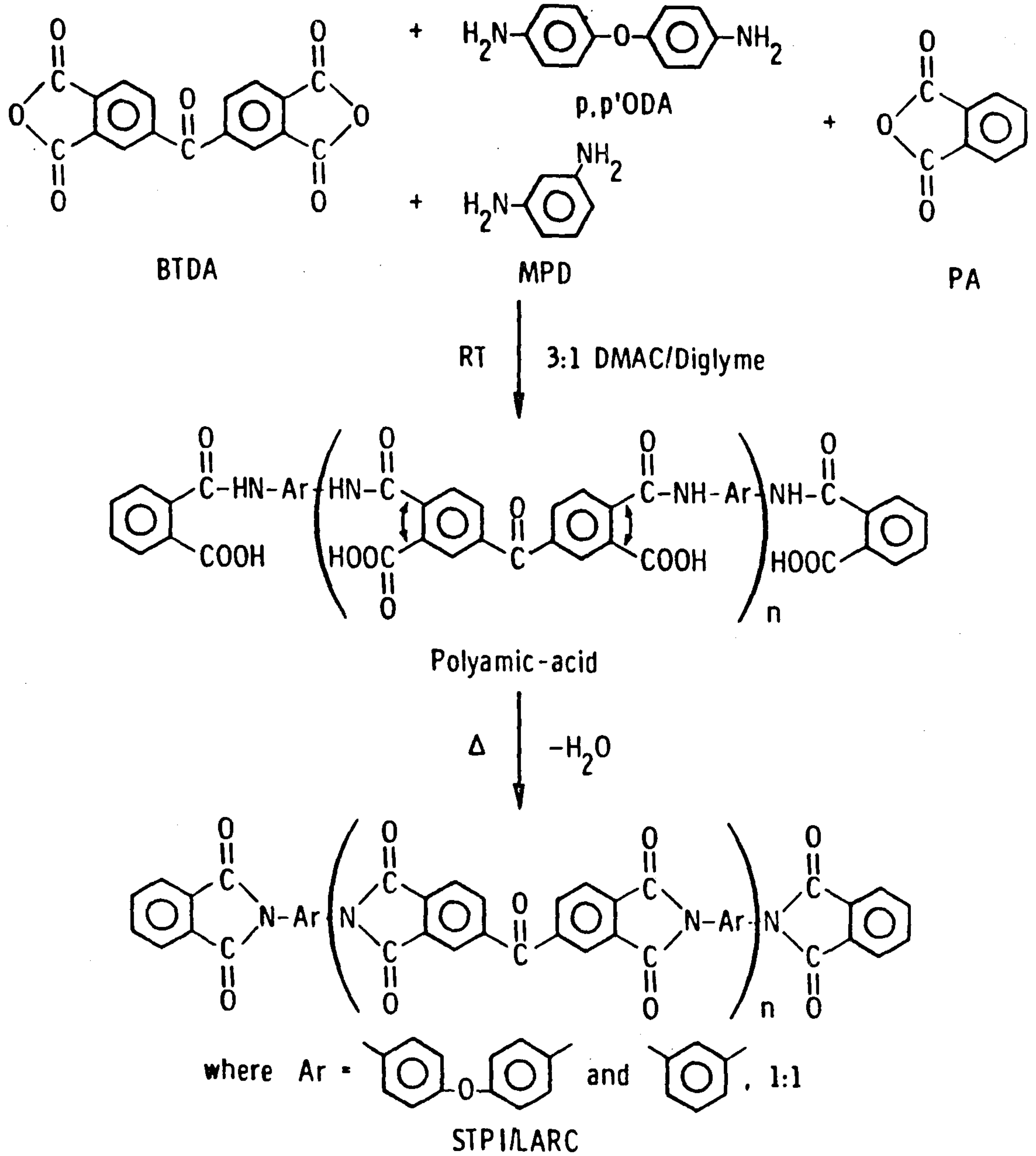


Figure 2. Reaction scheme for formation of STPI/LARC.

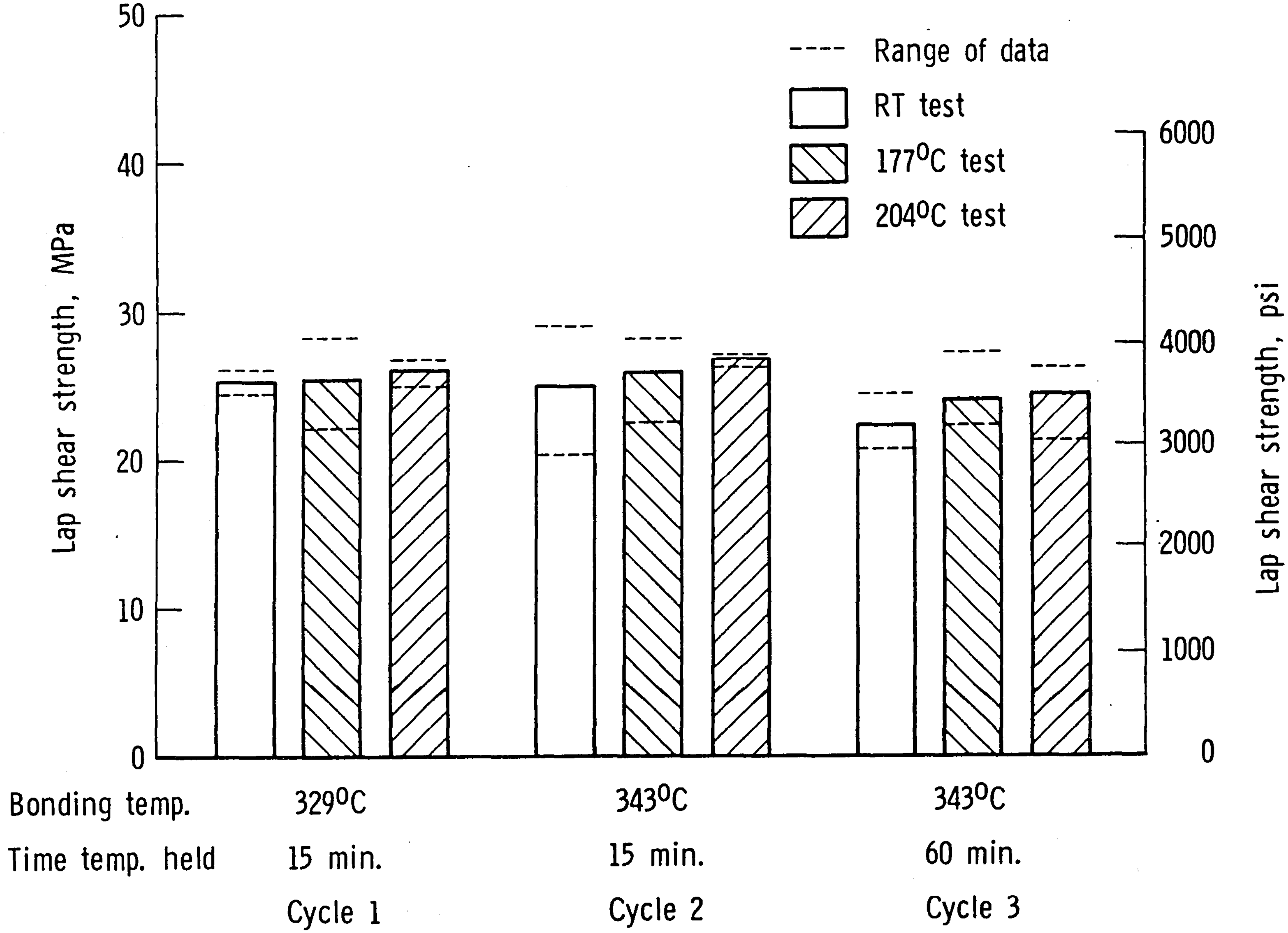


Figure 3. Effects of bonding temperature and time-temperature-held on lap shear strength of titanium bonded with STPI/LARC adhesive.

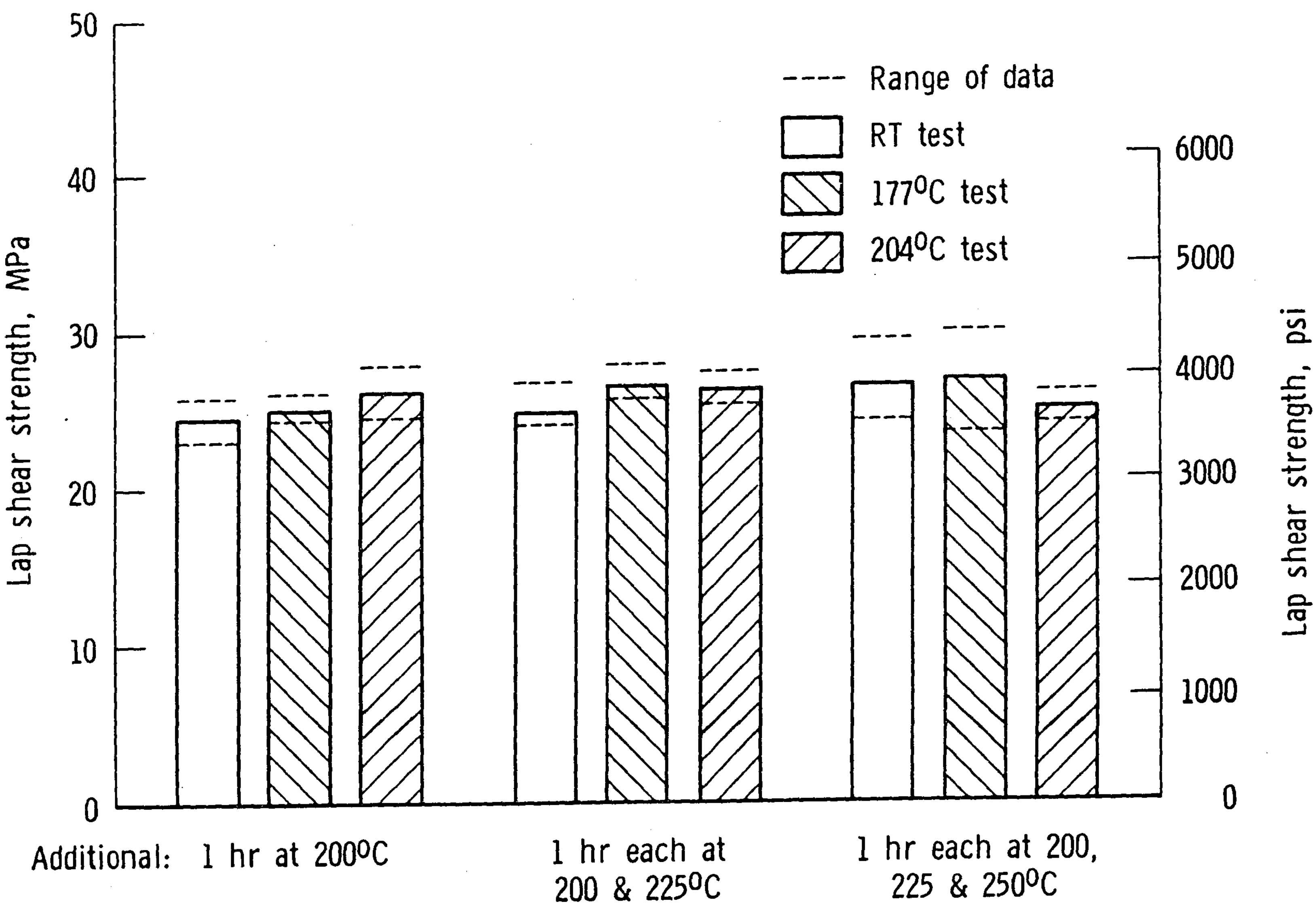


Figure 4. Effect on lap shear strength of additional heating (in air) of STPI/LARC adhesive tape prior to use for bonding titanium.

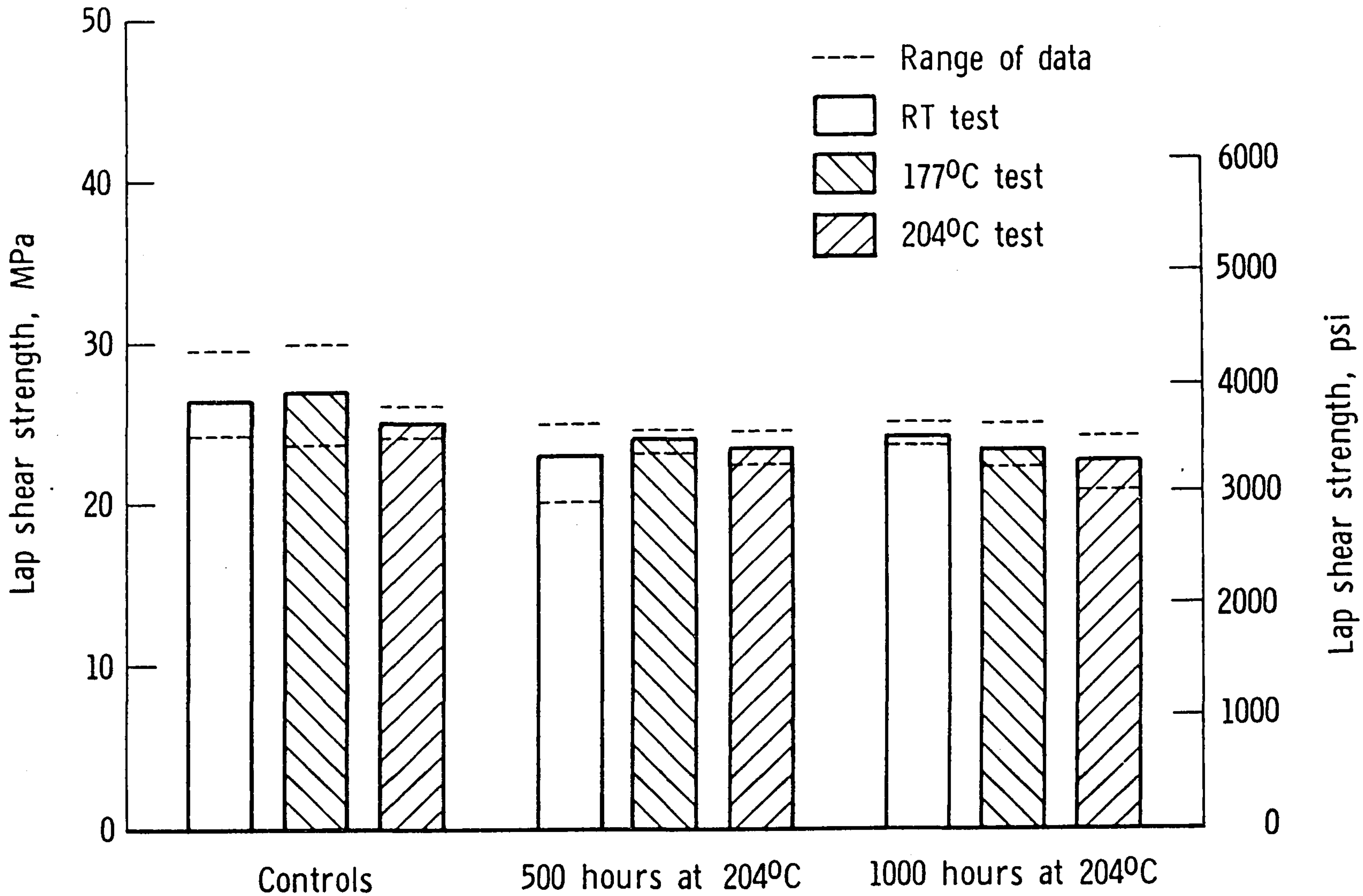


Figure 5. Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with STPI/LARC adhesive.

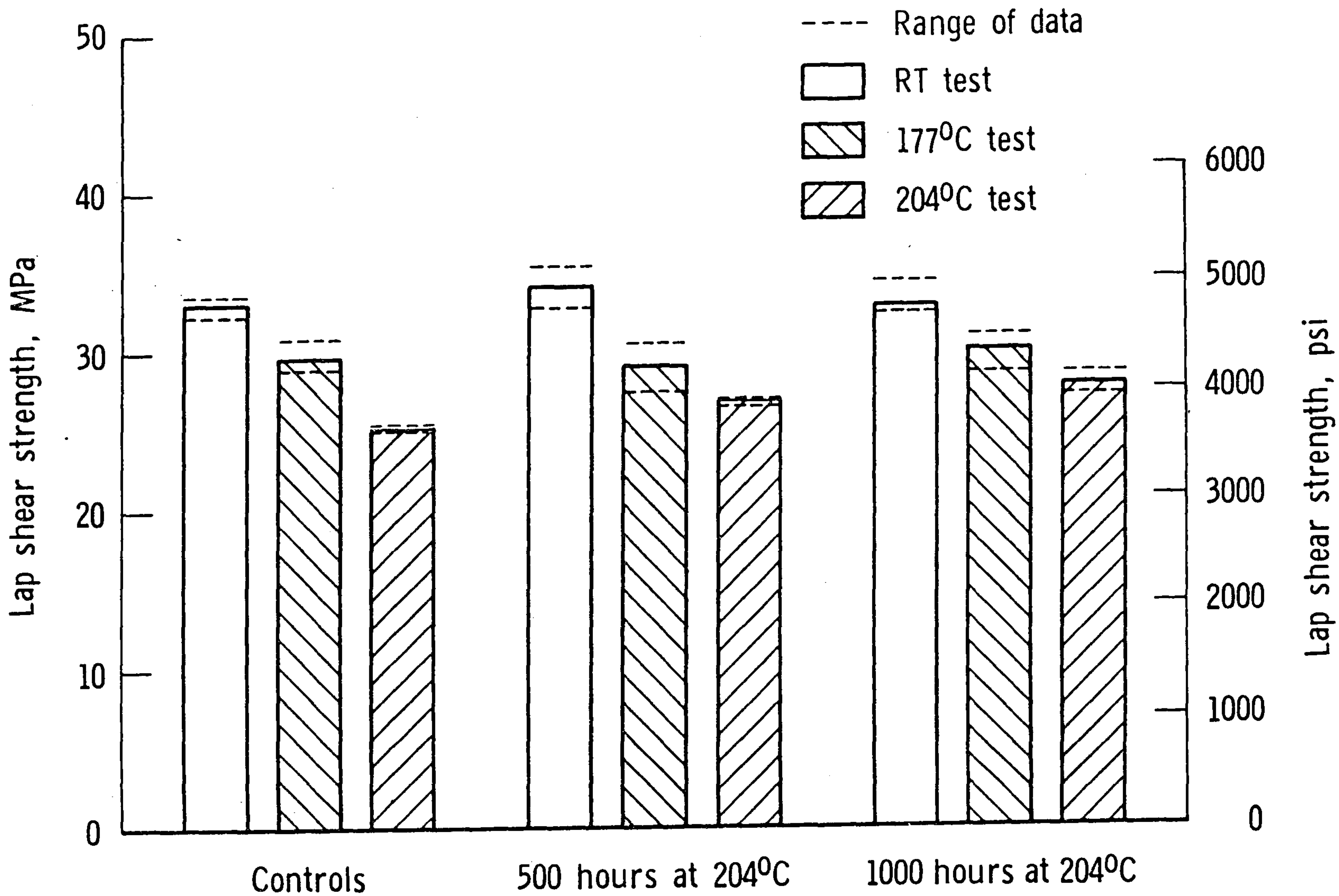


Figure 6. Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with LARC-TPI adhesive.

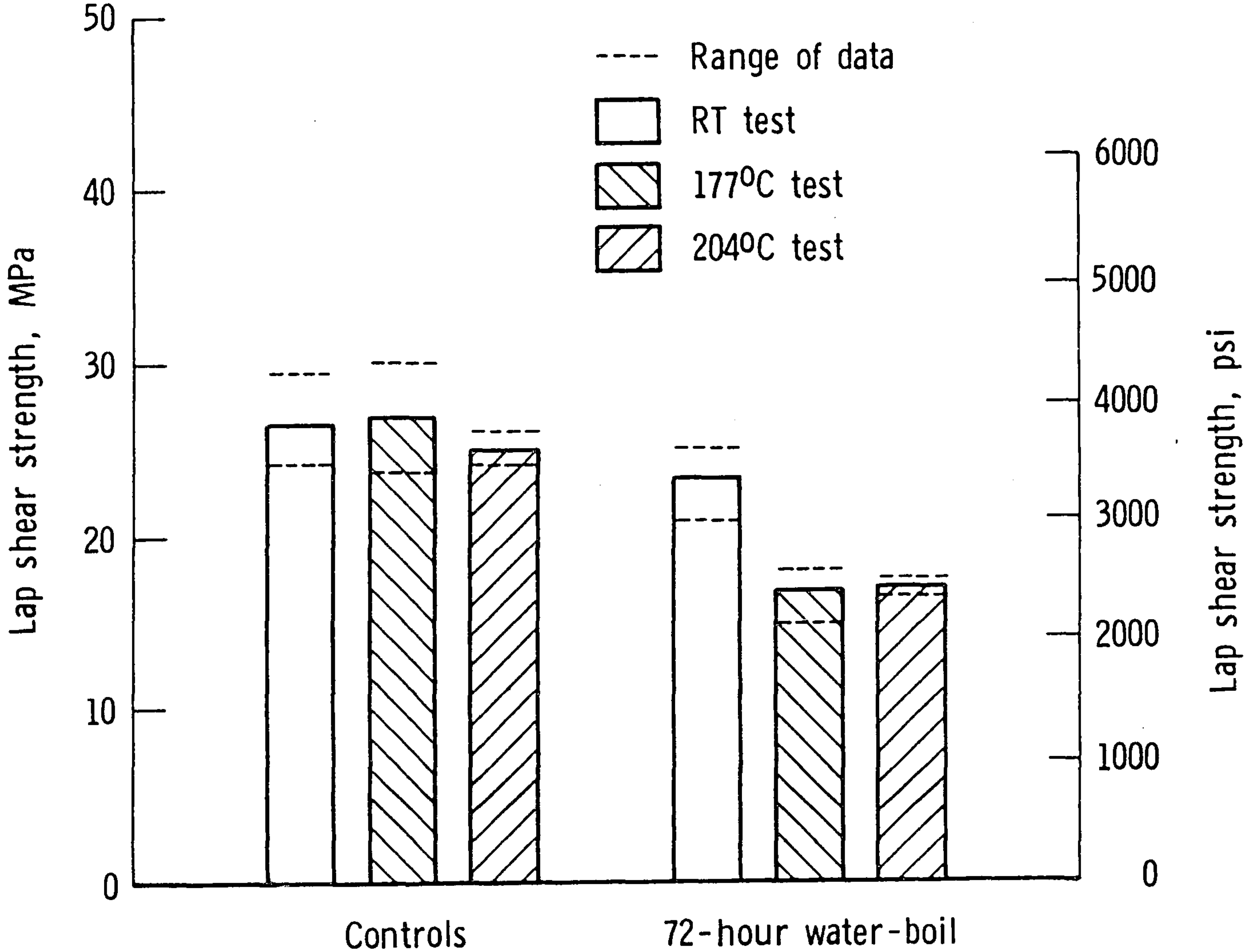


Figure 7. Effect of a 72-hour water-boil on lap shear strength for titanium bonded with STPI/LARC adhesive.

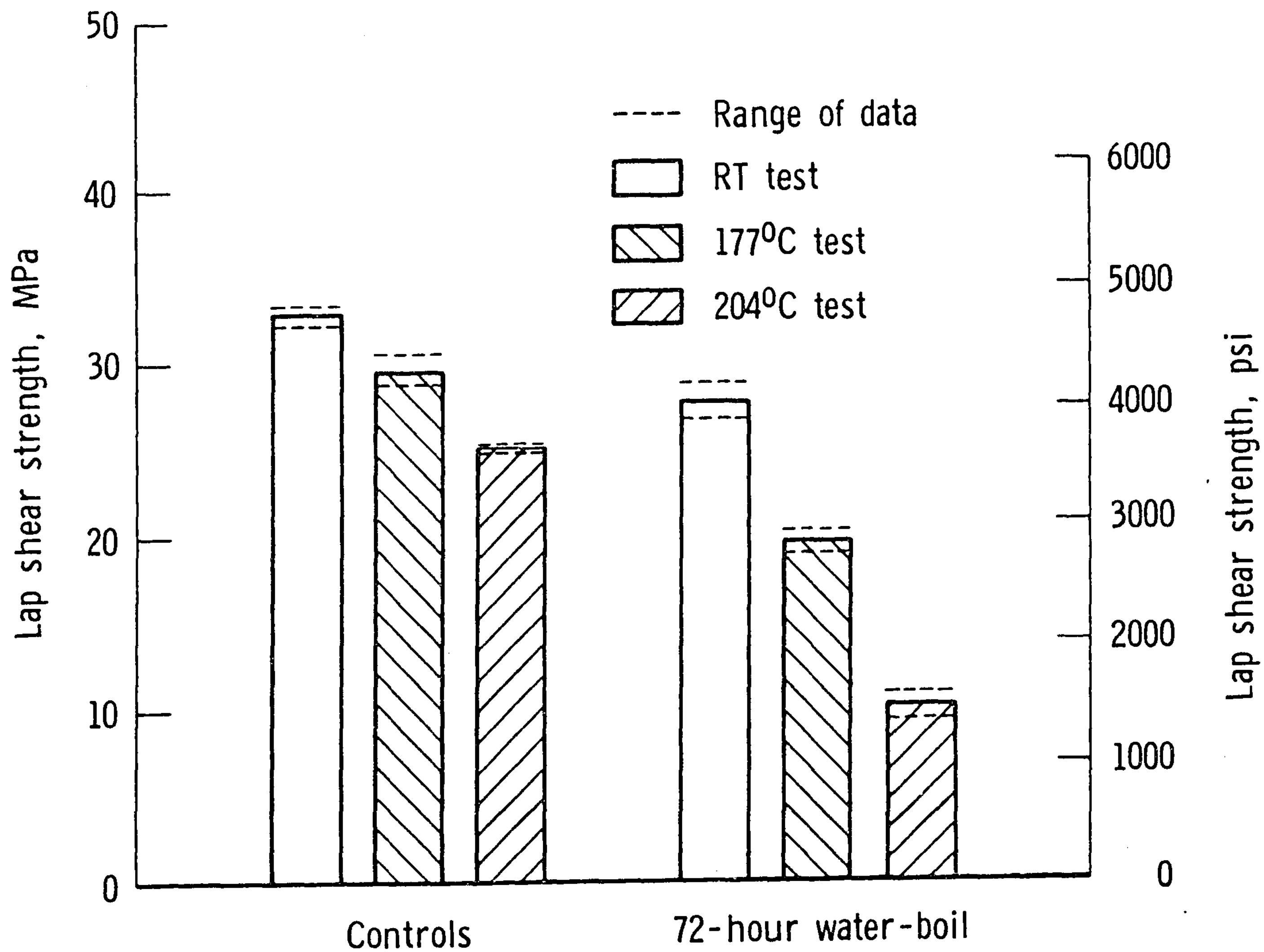


Figure 8. Effect of a 72-hour water-boil on lap shear strength for titanium bonded with LARC-TPI adhesive.

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16. Abstract

A copolyimide, STPI/LARC, was prepared from the reaction of 3,3'4,4'benzophenonetetracarboxylic dianhydride (BTDA), equimolar quantities of m-phenylenediamine and 4,4'-oxydianiline, and a small amount of phthalic anhydride to control the molecular weight. The processability and adhesive properties of STPI/LARC were compared to those of a commercially available form of LARC-TPI. LARC-TPI, a thermoplastic polyimide, from the reaction of BTDA and 3,3'-diaminobenzophenone, had previously shown promise as a high temperature structural adhesive.

Lap shear specimens were fabricated using adhesive tape prepared from each of the two polymers. Lap shear tests were performed at room temperature, 177°C, and 204°C before and after exposure to a 72-hour water-boil and to aging at 204°C.

17. Key Words (Suggested by Author(s)) Copolyimide, Polyimide, Adhesive, LARC-TPI, Thermoplastic	18. Distribution Statement Unclassified - Unlimited Subject Category 27

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